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A DEEPER INSIGHT INTO THE STRUCTURE AND ISOMERIZATION REACTIONS OF THE CYCLOPROPENYL-TYPE SYSTEMS

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Abstract—A complete set of stationary points of the cyclopropenyl cation and radical and that of the singlet and triplet states of the cyclopropenyl anion were investigated semiempirically. The Wiberg parametrization of the CNDO/2 method was used and the geometry of the systems under study was fully optimized. For the cation, radical and anion (in the case of the anion the triplet ground state and the singlet first excited state), one, three, one and six stationary structures were found, respectively. With each of the four types of systems only one stationary state lies in a real energy minimum. Some of the other structures found are activated complexes in the isomerization reactions which are of importance for derivatives of the parent systems. An unusual type of the Jahn–Teller distortion, specific for symmetric, cyclic systems, is reported.

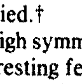
INTRODUCTION

For more than three decades after the Hückel's formulation of the conditions of the aromaticity[1] of cyclic conjugated systems, experimental and theoretical chemists dealt with systems possessing $4n+2$ electrons ("natural systems").[2] Only during the last few years has attention turned towards "unnatural" systems. Not only the parent systems (e.g. C_3H_3 , $C_5H_5^+$, C_7H_7 , . . . ; $C_3H_3^{\cdot}$, $C_5H_5^{\cdot}$, $C_7H_7^{\cdot}$, . . .) but also derivatives thereof have been the subject of theoretical and experimental studies. For example, it was found theoretically that the cyclopentadienyl cation possesses a planar triplet ground state (D_{5h})[3] while its first excited singlet state is non-planar. However, the structure of the excited state has not yet been unambiguously resolved.[4-7]

Systems of the cyclopropenyl type have been studied theoretically on many different levels of sophistication: HMO-LCI,[8] PPP,[9] EHT,[10] INDO,[11] MINDO/3,[12] *ab initio* (π-electronic approximation),[13] and *ab initio*.[14,15] Unfortunately geometries of the systems studied, except of that for the symmetric (D_{3h}) cation,[11] have not been fully optimized, and moreover, only selected structures were studied.†

High symmetry of these systems represents one of their interesting features. Systems possessing degenerate open shell frontier orbitals are subjected to the Jahn–Teller[16] distortion: presence of a many-fold symmetry axis can manifest itself by formation of a multi-dimpled potential energy surfaces. Liehr[17] discussed the nature of such surfaces qualitatively; to our knowledge, none of them has been studied quantitatively.

Theoretical structure investigation of the three oxidation steps **1–3** of the cyclic conjugated system C_3H_3, is the subject of this work.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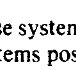
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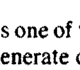
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The aim was to find all stationary points on the energy hypersurfaces of the species **1–3**. This was facilitated by a program which permits the automatic optimization[18,19] of molecular geometries. The nature of the individual stationary points was analyzed in terms of the calculated force constants matrix (FCM). Since the results were obtained by a semi-empirical quantum mechanical method, they are of a tentative nature.

EXPERIMENTAL

All calculations were performed by the CNDO/2 method parametrized according to Wiberg.[20] The open shell systems as well as the singlet and triplet states of the cyclopropenyl anion of the D_{3h} symmetry were calculated by the half-electron method.[21] The stationary points were found by a minimization of the total energy with respect to all coordinates of the studied system. FCM were calculated from the values of the gradient changes[19] and the corresponding changes of the coordinates. All the coordinates were changed stepwise by 5×10^{-13} m. Limited configuration interaction was used for the description of the singlet states of **3**; SCF wave function was allowed to interact with the lowest doubly excited configuration. We limited ourselves to the study of cyclic forms of the C_3H_3 system only in order to avoid the inherent weakness of the CNDO type method in describing cycle openings.

The output of the geometry optimization program was used for perspective depictions of optimized structures on a plotter. All calculations were performed on the IBM 370/135 computer.

RESULTS AND DISCUSSION

First we dealt with the structure determination of **1**, chiefly in order to verify the method used. In agreement with previous results (*cf* Refs 8–15) we found that the planar form **4** of D_{3h} symmetry was of lowest energy. Geometrical characteristics are summarized in Fig. 1. The CH bond length we obtained is nearly the same as that published in Ref. 11; our CC bond length is somewhat longer than that published previously[11] (1.418 Å). Our value would seem to be more correct because the Wiberg method is free of the inherent shortcoming of the INDO method which manifests itself by rather short bond lengths[22] for single bonds. The FCM of **4** is positive definite (all its eigenvalues are positive) which suggests that the structure found corresponds to a real minimum.

A slightly more complicated case concerns the struc-

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†In addition to the structures described in the present paper, flapped structures were found which were similar to our structures **12** and **13** found among others for the cyclopropenyl anion in studies by N. C. Baird, *J. Org. Chem.* **40**, 624 (1975).

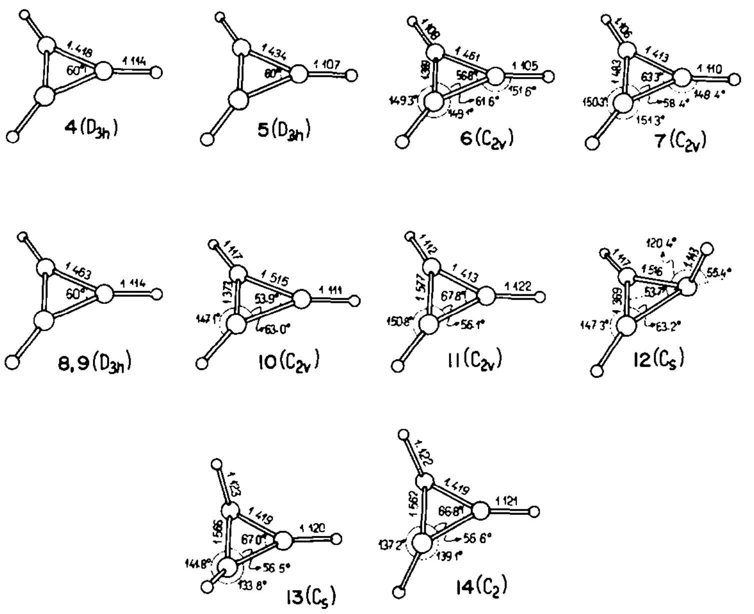


Fig. 1. Structure and geometry characteristics of stationary points of energy hypersurfaces belonging to the cyclopropenyl cation, radical and anion.

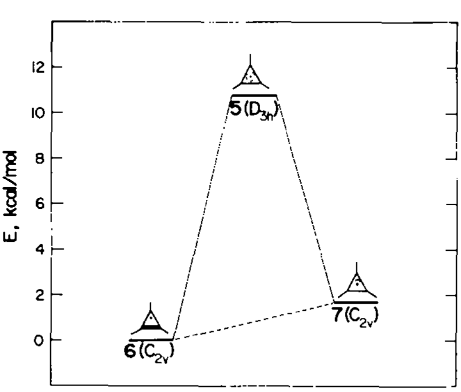
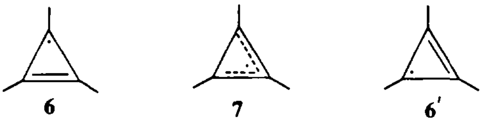


Fig. 2. Energy scheme of transitions among various structures of the cyclopropenyl radical. The full lines correspond to a one-direction "deactivation". Mutual transitions among the structures can be performed only along the dotted lines.

ture of the radical **2** because its antibonding doubly degenerate orbital is occupied by a single electron only. The sӯmmetric form **5** (D_{3h}) is subject to the Jahn–Teller distorsion giving the distorted structure **6** (C_{2v}) which is stabilized by 1.7 Kcal/mole in comparison to the other distorted structure **7** (C_{2v}) (Fig. 2). Clearly, the energy difference between the distorted forms is very small when compared to the energy difference between either the form **6** or **7** and the D_{3h} form **5** (10.8 or 9.1 Kcal/mole, respectively). The *ab initio* method[15] (without performing full geometry optimization) leads to a stable isomer, possessing C_{2v} symmetry, with the CCC angle of 72° and with a distortion energy of 12 Kcal/mole. Structure **6** possesses all positive eigenvalues of the FCM and is, therefore, a real minimum. An analogous analysis based on the FCM leads to the conclusion that the form **7** represents an activated complex since just one of the eigenvalues of the FCM is negative. From the analysis of the eigenvector belonging to this eigenvalue, it becomes evident that **7** corresponds to the saddle point on the reaction coordinate, which represents the migration of the short C–C bond of the form **6**:



6 **7** **6′**

Therefore, only one of both Jahn–Teller states represents a real minimum and it is the form **6**. Clearly, because of the C_3 symmetry axis of the parent radical **2** three equivalent forms of **6** can be formed. The potential surface is obviously a special case of the surface suggested by Liehr.[17] The transition among the forms **6** and **6′** does not occur via the state of the D_{3h} symmetry but is realized by one of the three possible forms **7**. Therefore, the energy barrier is smaller than the energy of the Jahn–Teller distorsion. Günthar *et al.*[23] found by the analysis of the ESR spectra of the cyclopropenyl radical that the inversion barrier was 0.57 kcal/mole. An attempt to interpret this barrier in terms of the *ab initio* value for the Jahn–Teller inversion (10.8 kcal/mole) failed. Our calculated value of the activation energy of the reaction amounts to 1.7 kcal/mole which agrees well with the above mentioned observed value 0.57 kcal/mole. Moreover, our value of the Jahn–Teller distorsion is close to the *ab initio* value (12.0 kcal/mole compared with 10.8 kcal/mole).

In the case of the anion **3**, the presence of two electrons in the doubly degenerate MO suggests that the ground state should be a triplet. Its geometric parameters (structure **8**) are given in Fig. 1. A similar behaviour can be expected for the excited states of the cyclopropenyl anion as found for the cyclopropenyl radical. Therefore, the form possessing the D_{3h} symmetry cannot be the activated complex in transitions between the distorted Jahn–Teller isomers and, moreover, only one of these two isomers corresponds a minimum on the energy hypersurface.

A vertical excitation of the form **8** (D_{3h}) leading to the lowest excited singlet state **9** (D_{3h}) is indicated in Fig. 3. Three of eigenvalues of the FCM of **9** are negative. An attempt to minimize the energy of this form leads to two planar distorted systems **10** and **11**. From the π-electronic point of view it is possible to consider the form **10** as ethylene weakly interacting with the methine anion (CH^-), while the form **11** appears to be a weakly perturbed allyl anion. The somewhat lower energy of the structure **10** is in accord with the assumed antiaromaticity of the cyclopropenyl anion.

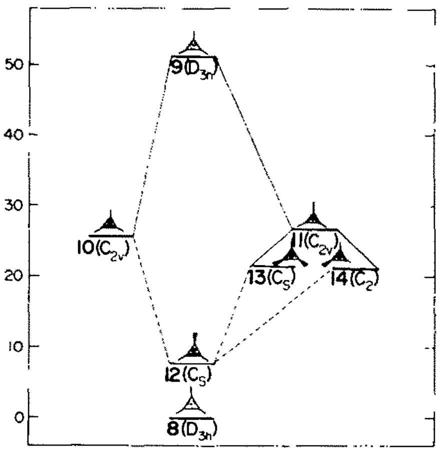


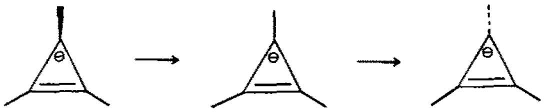
Fig. 3. Energy scheme of transitions among various structures of the cyclopropenyl anion (for further explanation see Fig. 2).

One negative eigenvalue belongs to the FCM of **10**. Therefore, the movement along the respective eigenvector leads to an energy decrease. This vector corresponds to the out-of-plane displacement of the hydrogen atom attached to the carbon atom situated opposite to the formal double bond. The displacement leads to the stationary point **12**. The FCM analysis shows that this should be a real minimum. The structure of the form **12** was treated theoretically also in Refs. 12, 14 and 15. In Ref. 14 the "out of plane" angle α was optimized; in addition, in Ref. 15 the C–C–C angle was optimized in part together with the angle α. There is a reasonable agreement between the value of 53.7° obtained for the angle α in this paper and the values found previously, namely 68°[14] and 60°.[15]

The form **11** is energetically somewhat less favourable than the form **10**, the difference being 0.9 kcal/mole. There is still another reason to believe that the form **11** is less favourable based on the fact that its FCM possesses two negative eigenvalues. Analogously as with the form **10** (i.e. by the FCM analysis), it is possible to reach the non-planar forms **13** and **14**. Both of these forms possess single negative eigenvalues of the FCM and do not represent minima on the energy hypersurface. Shifts according to the respective eigenvectors lead in both cases to a single stationary point corresponding to the form **12**. Therefore, this latter form appears to be the only stable isomer of $C_3H_3^-$ in the lowest excited singlet state (*cf* Fig. 3). Let us conclude that in addition to the simple Jahn–Teller distortion (like as with the cyclopropenyl radical) the symmetry plane in which all the atoms lie is not conserved in the case of the anion. We have here twenty-five stationary points which belong to six structures (**9–14**) instead of seven stationary points belonging to three structures of the radical. Therefore, the corresponding potential surface is more complicated than that suggested by Liehr[17] and can be considered to be an extension of the Jahn–Teller distortion. Let us add the number of distorted structures with the anion is equal to the double of internal coordinates of a molecule.

Forms **9** and **11** represent neither minima, nor saddle points and therefore it is possible to exclude their participation as activated complexes in C_3H_3 isomerizations. Clearly enough, these isomerizations can be proved experimentally with substituted derivatives only.

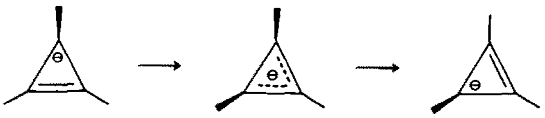
The activated complex for the "wagging coordinate" (inversion barrier of the "out-of-plane" hydrogen atom) is represented by the form **10**.



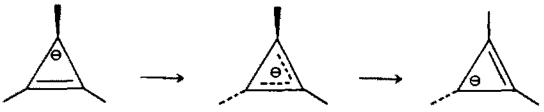
12 **10** **12′**

The inversion barrier calculated in this paper amounts to 25.7 kcal/mole. Considerably higher values were found in earlier calculations, namely 52.3[14] and 35.3[15] kcal/mol. In both cited papers an assumption was made that the form **9** was the activated complex; moreover with this assumption our calculation leads to the barrier height of 43.5 kcal/mole, which is a value lying between the two corresponding values noted above. Obviously, the pronounced decrease of the activation energy was reached by using the appropriate structure for the activated complex, i.e. the form **10** instead of **9**. With regard to the close resemblance of the forms **10** and **9**, we have to consider the obtained result as a serious warning against using geometries which are not fully optimized when studying problems like this.

The form **13** seems to be the activated complex for the double bond migration and the form **14** is the activated complex for the product **12″**, which can be also formally derived from **12**.



12 **13** **12″**



12 **14** **12″**

Clearly, in the case of the parent singlet anion the isomers **12**, **12′**, **12″** and **12‴** are indistinguishable. However, the opposite is true with deuterated or substituted isomers. Activation energies of reactions 3 and 4 are approximately the same (21.5 and 21.2 kcal mole) and are significantly smaller that the activation energy of the reaction 2 (25.7 kcal/mole). It is therefore possible to conclude that the migration of the formal double bond should be preferred relative to a simple hydrogen inversion.

The result obtained, according to which the symmetrical D_{3h} state does not represent the activated complex for the transition between Jahn–Teller isomers, agrees with the rules published by Murrell and Laidler.[24] Using such rules, the symmetry number of the form **5** is higher than that of the form **6**. Murrell-Laidler rules can be interpreted in our particular case as follows: molecules with at least a single C_3 symmetry axis possess degenerate eigenvectors of the FCM. If the displacement from the highly symmetrical state to distorted states proceeds along degenerate eigenvectors (which is obviously the case with our problems) and if the energies of the distorted states are lower than that of the parent (symmetrical) state, then the eigenvalues belonging to these eigenvectors are negative. However, a system whose FCM possesses two or more negative eigenvalues, cannot be a transition state. This case will occur when, because of the parent system, the Jahn–Teller distorsion can proceed by several equivalent ways. Then always one of the conjugated Jahn–Teller isomers is a real minimum, whereas the other represents an activated complex. Since the Jahn–Teller isomers can be obtained by several ways, it results in several equivalent structures of the first and second type. Structures of the second type are activated complexes for mutual transformations of structures of the first type.

Before finishing the discussion let us comment on the influence of the limited configuration interaction (LCI) on the energies of the singlet states of the system **3**. The CI energy lowering amounts to 2.28 and 5.35 kcal/mole for the planar forms **10** and **11**, 4.43 and 5.21 kcal/mole for the forms **13** and **14** and only 1.59 kcal/mole for the stable isomer **12**. After the inclusion of CI the activation energies for reactions 2–4 increase, the order of their feasibility remains unchanged, however. The unimportance of the lowest doubly excited state for the description of isomers **10–14** is seen also from the values of squares of the expansion coefficients which belong to the doubly excited configurations. Whereas this amounts to 0.5 for the structure **9**, it decreases to 0.011, 0.031, 0.025 and 0.030 for the forms **10**, **11**, **13** and **14**, and is only 0.006 for the stable form **12**. Therefore, the SCF approximation should be sufficient for such a study. The high separation of the states, which are degenerate with the D_{3h} symmetry, caused by the relative small Jahn–Teller displacement is probably the reason for the large energy lowering when going from the system **9** to any of the systems **10–14**.

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